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Supporting Information

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Reversible Electrocatalytic Production and Oxidation of Hydrogen at Low Overpotentials by a Functional Hydrogenase Mimic**

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Supporting Information

I. General Experimental Procedures.

General: Unless otherwise noted, all reactions and manipulations were carried out under a N_2 atmosphere using standard Schlenk and high-vacuum techniques, or in a Vacuum Atmospheres inert atmosphere glovebox (N_2) at ambient temperature. Glassware was dried for a minimum of 8 h at 150 ^oC. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for ^1H) at 20 °C unless otherwise noted. All NMR chemical shifts are reported as δ in parts per million (ppm). All ^1H chemical shifts have been internally calibrated to residual protiated solvent, and the chemical shifts are reported in parts per million downfield from tetramethylsilane. The $^{31}P\{^1H\}$ NMR spectra are referenced to external phosphoric acid. The $^{13}C\{^1H\}$ NMR spectra were calibrated using the resonance from the solvent.

All electrochemical experiments were carried out under an atmosphere of nitrogen, or hydrogen as indicated, in 0.2 M Et_4NBF_4 or 0.2 M *n*-Bu_4NPF_6 solutions of acetonitrile. Cyclic voltammetry experiments were performed with a CH Instruments model 660C potentiostat at a scan rate of 0.050 Vs^{-1}. Ferrocene was used as an internal standard, and all potentials are referenced relative to the ferrocenium/ferrocene couple. Glassy carbon was used as the working electrode.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Acetonitrile and was passed through a column of activated alumina under N_2 pressure. Deuterated solvents were purchased from Cambridge Isotope Laboratories. CD_3CN and was vacuum transferred from P_2O_5. CD_2Cl_2 was vacuum transferred from CaH_2. 4-cyanoaniline was recrystallized from absolute ethanol. 4-cyanoanilinium tetrafluoroborate[1] and phenyl bishydroxymethylphosphine[2] was prepared according to literature procedures.

II. Synthesis

[($P_2^{Ph}N_2^{CH2CH2OMe}$)$_2$Ni] (2). Phenyl bishydroxymethylphosphine ($PhP(CH_2OH)_2$) (3.90 g, 22.9 mmol) was added to a 100 mL Schlenk flask followed by 40 mL of absolute ethanol, pre-sparged for 30 minutes with N_2. The mixture was stirred while heating to 70 ^oC in an oil bath. The 2-methoxyethylamine (1.72 g, 22.9 mmol) was added to a vial followed by 10 mL of absolute ethanol. The amine solution was sparged with N_2 for 11 minutes and then added dropwise to the Schlenk flask via syringe. The reaction solution was stirred at 70 ^oC for 5 h, after which point the reaction mixture was allowed to slowly cool to room temperature overnight. An emulsion formed and the upper layer was removed with a pipette, exposing the solution temporarily to air. The bottom layer was dried under vacuum, yielding a thick oil, that

was used without further purification. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -36.76 (s, 33%), -41.72 (s, 14%), -46.33 (s, 4%), -48.88 to -47.28 (br peak, 12%), -50.79 (s, 6%), -65.95 to -70.57 (br peak, 31%). The ligand mixture (2.18 g, 5.21 mmol) was placed into a vial equipped with a stir bar and ~ 5 mL acetonitrile was added. $[(CH_3CN)_6Ni][BF_4]_2$[3] (1.24 g, 2.59 mmol) was added to a 100 mL Schlenk flask and dissolved in ~ 5 mL acetonitrile. The nickel solution was then added to the ligand solution. The entire contents of the solution were transferred to the Schlenk flask by washing the vial with ~ 20 mL acetonitrile and ~ 3 mL THF. The total volume of the solution was ~ 40 mL. The reaction mixture was stirred at room temperature overnight. After this time, the reaction solution was sparged with H_2 for 15 minutes and then TMG (0.70 mL, 5.54 mmol) was added dropwise via syringe over the course of 5 min while continuously sparging the solution with H_2; after complete addition, H_2 was sparged for an additional 5 minutes. The Schlenk flask was stored at −80 °C in the freezer for 24 hours (this likely is not necessary). After warming to room temperature, the mother liquor was removed from the yellow precipitate via cannula transfer. The precipitate was washed with 10 mL of acetonitrile and dried under reduced pressure to give 1.10 g of a yellow solid (47% yield). Typical yields range from 22 to 47%. ^{1}H NMR (C_6D_6): δ 2.88 (br t, *J* = 5.9 Hz, 8H, NC*H*$_2$CH$_2$), 3.04 (d, *J* = 11.2 Hz, 8H, PC*H*$_2$N), 3.08 (s, 12H, OC*H*$_3$), 3.34 (br t, *J* = 5.8 Hz, 8H, NC*H*$_2$CH$_2$), 3.35−3.39 (m, 8H, PC*H*$_2$N), 7.11 (t, *J* = 7.4 Hz, 4H, *aryl*), 7.22 (t, *J* = 7.4 Hz, 8H, *aryl*), 7.88 (br s, 8H, *aryl*). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ −2.08. $^{13}C\{^{1}H\}$ NMR (THF−d_8): δ 58.60 (m, P*C*H$_2$N), 58.77 (s, O*C*H$_3$), 61.92 (m, N*C*H$_2$CH$_2$OMe), 71.51 (s, NCH$_2$*C*H$_2$OMe), 128.25 (s, aryl), 128.77 (s, aryl), 131.89 (m, P−C−*C aryl*), 144.19 (m, P−*C aryl*). Anal. Cald for $C_{44}H_{64}N_4NiO_4P_4$: %C 59.01 %H 7.20, %N 6.26. Found %C 59.12, %H 7.06, %N 6.26.

$[(P_2^{Ph}N_2^{CH2CH2OMe})_2Ni][BF_4]_2$ (1). The complexes $(P_2^{Ph}N_2^{CH2CH2OMe})_2Ni$ (**2**, 0.212 g, 0.237 mmol) and ferrocenium tetrafluoroborate (0.130 g, 0.476 mmol) were added to two separate vials and 2 mL of acetonitrile was added to each vial. The ferrocenium solution was added to the Ni^0 slurry by pipette and the reaction was stirred overnight. The reaction mixture was concentrated until ferrocene began to precipitate, at which point the solution was cooled to −35 °C. The mother liquor was rapidly removed with a pipette and the precipitate was washed with 1 mL cold acetonitrile. The acetonitrile wash was combined with the mother liquor, and the volatile materials were removed under vacuum. The resulting red solid was slurried in 20 mL Et_2O and stirred vigorously overnight. The slurry was then filtered and the solid dissolved in CH_2Cl_2 (~ 15 mL), transferred to a vial and concentrated to dryness yielding a red−orange solid. Yield: 250 mg (99%). ^{1}H NMR (CD_2Cl_2): δ 3.11 (br t, *J* = 4.4 Hz, 8H, NC*H*$_2$CH$_2$), 3.36 (s, 12H, OC*H*$_3$), 3.39 (d, *J* = 13.8 Hz, 8H, PC*H*$_2$N), 3.65 (br t, *J* = 4.4 Hz, 8H, C*H*$_2$OMe), 3.89 (d, *J* = 13.0 Hz, 8H, PC*H*$_2$N), 7.14 (br s, 8H), 7.22 (br t, *J* = 6.9 Hz, 8H, *aryl*), 7.40 (br t, *J* = 7.2 Hz, 4H, *aryl*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ −1.38. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 59.2 (s, O*C*H$_3$), 60.7 (t, 5.1

Hz, P*C*H_2N), 71.0 (s, NCH_2*C*H_2OMe), 130.4 (br s, *aryl*), 131.8 (s, *aryl*). Anal. Cald for $C_{44}H_{64}B_2F_8N_4NiO_4P_4$: %C 49.43 %H 6.03, %N 5.24. Found %C 49.11, %H 6.22, %N 5.24.

$^{31}P\{^1H\}$ NMR of 2A, 2B, 2C, and 3. 2A: $^{31}P\{^1H\}$ NMR (CD_3CN): δ 10.7 ppm. **2B**: $^{31}P\{^1H\}$ NMR (CD_3CN): δ 11.3, −14.1 ppm. **2C**: $^{31}P\{^1H\}$ NMR (CD_3CN): δ −15.1 ppm. **3**: −18.9 ppm.

^1H NMR of N-H in 2A, 2B, and 2C. 2A: ^1H NMR (CD_3CN): δ 6.23 ppm. **2B**: ^1H NMR (CD_3CN): δ 13.27, 6.05 ppm. **2C**: ^1H NMR (CD_3CN): δ 13.35 ppm.

III. Thermodynamic Studies

Determination of K_{eq} for H_2 Addition to 1. A solution of **1** in acetonitrile (~ 450 µL, 15.3 mM, 7 µmol) was added to an NMR tube via syringe, and covered with a septum. Hydrogen was then sparged through the solution at 23 °C for 5 minutes under 1 atm. The NMR spectrometer's temperature was calibrated to 23 °C using an ethylene glycol standard. Quantitative ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained by measuring the T_1 values for both the proton and phosphorus nuclei and then ensuring that the delay time was at least 5 x T_1. For both the ^1H and $^{31}P\{^1H\}$ NMR spectra, the longest T_1 was < 3 s. An equilibrium constant of K_{eq} = 0.24(2) atm^{-1} was determined by ^1H NMR and K_{eq} = 0.27 atm^{-1} by $^{31}P\{^1H\}$ NMR spectroscopy for the addition of H_2 to **1** to form the isomers **2A**, **2B** and **2C**.

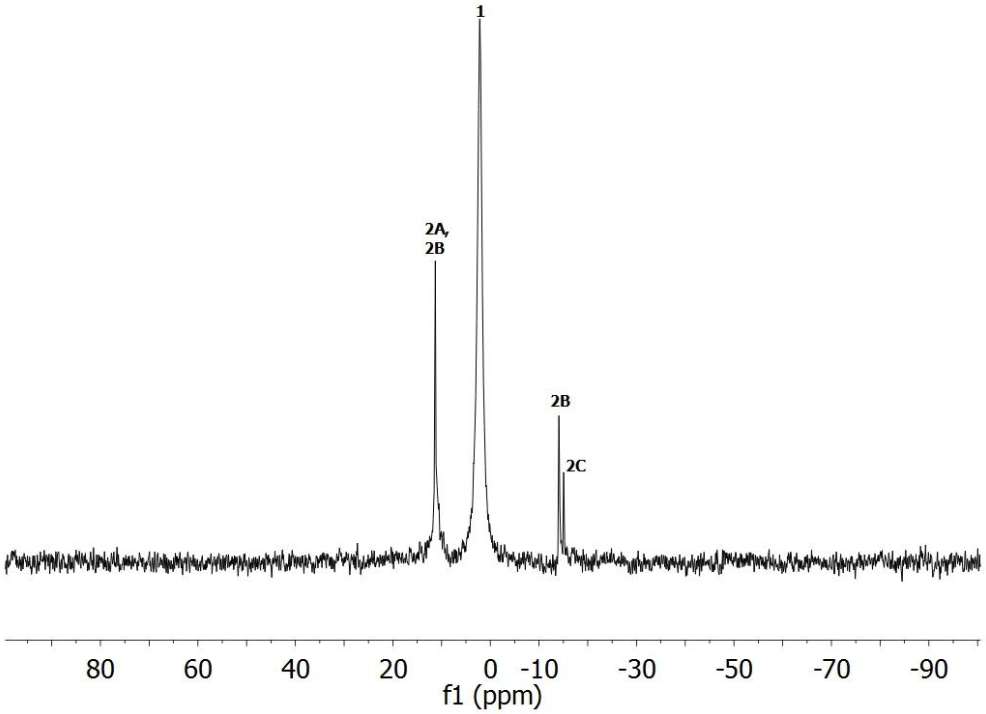

Figure S1. $^{31}P\{^1H\}$ NMR of **1** under an atmosphere of hydrogen, with products **2A**, **2B**, and **2C** in CD_3CN at 23 °C.

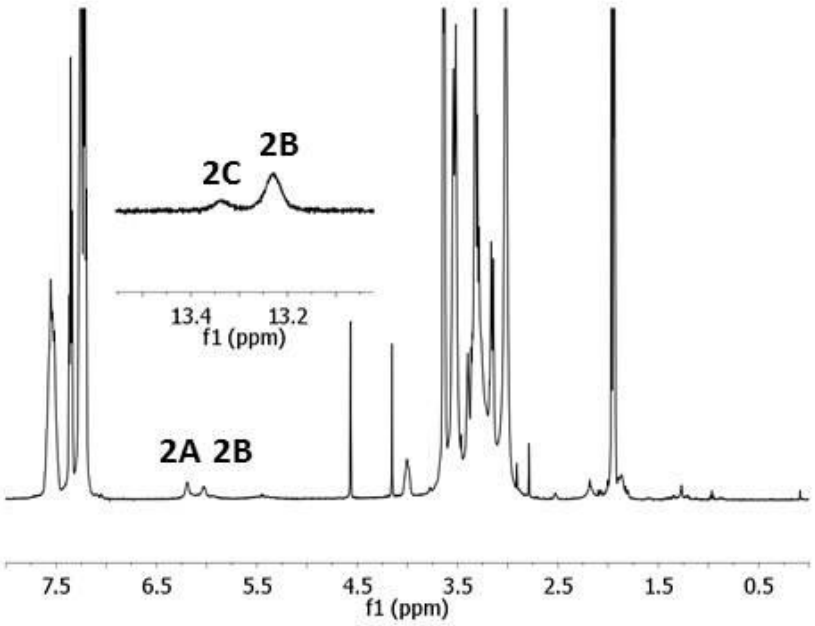

Figure S2. ^{1}H NMR of **1** under an atmosphere of hydrogen, with products **2A**, **2B**, and **2C** in CD_3CN at 23 ^{o}C.

pK_a Determination of 3. A solution (400 µL) of **1** (15.3 mM, 6.12 µmol) in CD_3CN was syringed into an NMR tube followed by an additional 200 µL of CD_3CN, yielding an initial solution concentration of 10.2 mM for **1**. To this solution was added two aliquots of 4-cyanoanilinium tetrafluoroborate (80 mM) in CD_3CN, corresponding to 120 µL and 110 µL. A ^{1}H NMR and ^{31}P{^{1}H} NMR spectrum was recorded for each aliquot. Integration of the ^{31}P{^{1}H} NMR was used to determine the relative concentration of **1** and the di−protonated species, **3**. The ratio of 4−cyanoanilinium tetrafluoroborate and 4−cyanoaniline was determined from the chemical shift of the aromatic resonances of the ^{1}H NMR spectra. The base and its conjugate acid rapidly exchange protons at room temperature, producing a chemical shift that is the weighted average for the chemical shifts of 4-cyanoanilinium tetrafluoroborate and 4-cyanoaniline. To demonstrate that the reaction was at equilibrium, three aliquots of 4-cyanoaniline (0.98 M) were added to the NMR tube, corresponding to 10 µL, 5 µL and 25 µL. After the first addition of 4-cyanoaniline, the solution was allowed to sit overnight and a second series of ^{1}H and ^{31}P{^{1}H}NMR spectra were acquired. The same ratio was observed to be within experimental error and demonstrates that the solution was indeed at equilibrium when it was initially recorded. An equilibrium constant of K_{eq} = 0.2 (± 1) was determined for deprotonation of **3** by 4-cyanoaniline. The use of this K_{eq} value in combination with the known pK_a of 4-cyanoanilinium tetrafluoroborate (7.0)[4] was used to determine the average pK_a value of 7.3 for **3**.

IV. Electrochemical Experiments

Catalytic Proton Reduction with 4−Cyanoanilinium Tetrafluoroborate. 1.9 mg (1.8 μmol) of **1** and ~ 1 mg of ferrocene were dissolved in 2.0 mL of 0.21 M Et_4NBF_4 to make a 0.8 mM solution of **1**. A cyclic voltammogram was recorded to give the two observed one electron reversible couples. A 0.59 M solution of 4−cyanoanilinium tetrafluoroborate was prepared by dissolving 159 mg (0.77 mmol) of the acid in 1.3 mL of acetonitrile. A total of 10, 20, 40, and 80 μL of the acid solution were added to the catalyst solution, and a cyclic voltammogram was recorded after each addition.

Reversible Catalysis in a Buffered Solution. Compound **1** (2.3 mg, 2.2 μmol) was placed into a vial and dissolved in 1.5 mL of 0.20 M *n*-Bu_4NPF_6 acetonitrile solution. An initial cyclic voltammogram was acquired under N_2 and in the absence of acid. The solution was titrated with 25 μL aliquots of a 1:1 molar ratio of 4-cyanoaniline : 4-cyanoanilinium tetrafluoroborate (0.356 M 4-cyanoaniline and 0.359 M 4-cyanoanilinium tetrafluoroborate) up to a total of 125 μL. In between each addition, a cyclic voltammogram was recorded. Upon complete addition, the solution was alternately sparged with H_2 and N_2 and a cyclic voltammogram was acquired under the different gas atmostpheres.

Controlled−Potential Coulometry. A 250 mL three−necked flask containing two threaded ports was charged with *n*-Bu_4NPF_6 (2.34 g, 6.0 μmol), 4-cyanoanilinium tetrafluoroborate (0.421 g, 2.0 mmol), **1** (11 mg, 0.01 mmol), ferrocene (2 mg, 0.01 mmol), acetonitrile (20 mL) and a stirbar. A counter electrode consisting of a coiled nickel−chromium wire was immersed in a 0.20 M *n*-Bu_4NPF_6 acetonitrile solution containing a fine frit at the end. The working electrode consisted of a cylinder of reticulated vitreous carbon (1 cm diameter by 2.5 cm length) that was connected to a stainless steel rod through. The reference electrode consisted of a silver wire immersed in a 0.20 M *n*-Bu_4NPF_6 acetonitrile solution along with a Vycor frit. A 1 mm glassy carbon working electrode was connected with copper wiring and threaded through a septum. The remaining ports were sealed with stoppers. The working and counter electrodes went through two of the 24/40 joints, the third 24/40 joint contained the septum with the 1 mm working electrode threaded through it. The reference electrode went through one of the threaded ports. The remaining threaded port was sealed with a glass rod. After 34.4 C were passed at –0.73 V vs the ferrocenium/ferrocene couple, a sample of the headspace was removed and analyzed by gas chromatography for hydrogen, demonstrating that 0.18 mmol of H_2 was produced with a current efficiency of 101 ± 5% This yields a TON = 18 and demonstrates that **1** is indeed a catalyst for H_2 production.

Catalytic Deuterium Oxidation with a Chemical Oxidant. 600 μL of a 0.94 mM solution of **1** (0.56 μmol) in CH_3CN was added to an NMR tube, along with 85 μL of a 380 mM solution of ferrocenium tetrafluoroborate (32 μmol) and 5 μL of 2,6-lutidine (43 μmol). The

solution was sparged with 1 atmosphere of deuterium gas for 3 minutes, but the reaction was visually complete after 2 minutes. Afterwards, 25 µL of a 22 mM C_6D_6 (0.55 µmol) in CH_3CN was syringed into the solution in the NMR tube. The amount of oxidized deuterium was determined by ^2H NMR using the C_6D_6 as an internal standard and integrating the N-D resonance relative to the C_6D_6 signal. This yields a TON for deuterium oxidation of 28 and demonstrates that **1** is a catalyst for hydrogen oxidation.

V. References:

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